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# Effect of drying time of 3-methacryloxypropyl-trimethoxysilane on the shear bond strength of a composite resin to silica-coated base/noble alloys

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## KEYWORDS

Silane coupling agents;  
Shear bond; Base alloys;  
Noble alloys; Material  
testing

**Summary Objectives.** In this in vitro study, the effect of various drying (surface reaction) times of a commercial silane, other than that recommended by the manufacturer (at least 5 min), on the bond strength between the resin composite and silica coated base and noble alloys was evaluated.

**Methods.** A total of 112 disc specimens (9 mm diameter and 0.5 mm thickness) were cast out of two types of alloy designed for ceramic firing, one of which was a noble (Degunorm) (gold-silver-platinum) and the other a base alloy (Wiron 99) (nickel-chromium-molybdenum). The specimens were assigned to two main groups according to each alloy type. These two main groups were further divided into seven subgroups, having eight specimens each. The specimens of both alloy types were air-abraded with 30  $\mu$ m silica (SiO<sub>2</sub>) coated alumina (Al<sub>2</sub>O<sub>3</sub>) (CoJet<sup>®</sup>-Sand, ESPE, Seefeld, Germany). The conditioned surfaces were coated with 3-methacryloxypropyltrimethoxysilane (MPS) and were allowed to react and dry for 1, 2, 3, 4, 5, 6, and 7 min, respectively, before the opaquer was applied. Immediately after the waiting periods for the silane to dry, first opaquer and then resin composite were applied. After storage in water for 30 days at 37 °C and thermocycling (5000 cycles, 5-55 °C), shear tests were performed using the universal testing machine at a crosshead speed of 0.5 mm/min.

**Results.** Analysis of data showed no significant difference in bond strength for any silane drying and reaction period for both base and noble alloys between 1 and 7 min (ANOVA,  $P = 0.05$ ) (Degunorm: 5.8-7.4 MPa and Wiron 99: 7.2-10.2 MPa, respectively). Bond strengths of resin composite to base alloys were significantly higher than those to noble alloys at 2, 3 and 5 min ( $P = 0.0045$ ,  $P = 0.05$ ,  $P = 0.002$ , respectively).

**Significance.** In order to optimize the flow of laboratory work, the silane solution drying time might be reduced to 1 min for both base and noble alloys.

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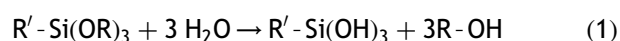
## Introduction

Silane coupling agents (organic silicon com-

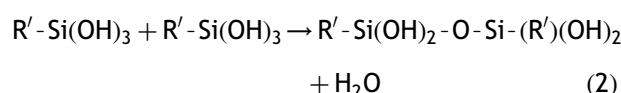
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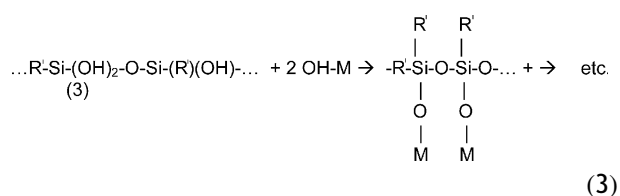
pounds), adhesion promoters, used in dentistry were at first vinyltrimethoxysilane and subsequently mainly 3-methacryloxypropyltrimethoxysilane (MPS).<sup>1-4</sup> These trialkoxyorganosilanes (hereinafter: silanes) have an organic functional radical (R', e.g. vinyl- or methacryloxypropyl) that can co-polymerize with the composite resin, and they have also three alkoxy groups (methoxy-O-CH<sub>3</sub>) ready to hydrolyze and then to react with surface hydroxyl groups on an inorganic substrate. The functional alkoxy groups react acid catalysed in aqueous alcohol solution to form at the first stage (i.e. hydrolysis) intermediate acidic silanol groups (-Si-OH):



The silanol groups then condense to form dimeric (and then oligomeric) molecules



In the next fast step, they form a three dimensional highly crosslinked siloxane (-Si-O-Si-) layer with covalent bonds, and also -Si-O-M (M = metal) bonds with the basic hydroxyl groups on the metal substrate surface. Water is eliminated in this reaction.<sup>5,6</sup>



Commercial dental silanes are typically prehydrolyzed, ready for use.

Recent advances in silane coupling agents appear to enhance bond strength by promoting a chemical bond between composite resin and porcelain.<sup>7,8</sup> The system of bonding composite resin to dental porcelain with a silane solution produced reliable bonds. It was thought to be an effective method for intraoral repair of fractured or chipped ceramic restorations. However, this report in the 1970s by Newburg et al.<sup>9</sup> suffered from difficulties at first, because of the instability of the silane solutions used to prepare the ceramic surface. Commercially available silane coupling agents have been steadily improved demonstrating higher bond strengths. Silanes are also applied as surface treatment agents for fillers (e.g. silicates, short E-glass fibres) in dental restorative composites, in order to modify the filler surface and bond the filler matrix firmly to the resin medium of the composite.<sup>10</sup>

A novel technique based on tribochemical silica coating provides micromechanical retention, utilizing air-particle abrasion, as well as a physicochemical adhesion between the resin composite and the silanized ceramic or alloy substrate.<sup>11</sup> The use of a silane coupling agent requires an absolutely dry environment. It is a prerequisite for the tribochemical bonding process between the silica coated surface and/or the opaque layer to develop a reliable bond between the dental ceramic, alloy and the composite.<sup>12,13</sup> The silanol groups bond chemically to the hydroxyl groups on the silicon dioxide surface, and water is released (see reactions (1)-(3) above). Ethanol and water in silane solution are released in the reaction and they evaporate.<sup>14</sup>

The recommended waiting period for drying of the silane is sometimes not easy to achieve in clinical practice when humidity cannot be controlled in the mouth or in the dental laboratory when ambient humidity exists. In this study, the effect of various drying times, other than that recommended by the manufacturer (at least 5 min) was evaluated on the bond strength a resin composite to silica coated base or noble alloys.

## Materials and methods

A total of 112 disc specimens (56 per alloy group) (9 mm diameter and 0.5 mm thickness) were prepared out of a wax sheet (Gebdi Dental Products GmbH, Engen, Germany) parallel to the surface using a copper ring. The wax samples were invested in a phosphate-bonded investment (Bellavest T<sup>®</sup>, BEGO, Bremen, Germany). Two types of alloys designed for ceramic firing, one of which was a noble, gold-silver-platinum, (Degunorm, Degussa, Hanau; Germany) and the other a base alloy, nickel-cobalt-molybdenum (Wiron 99, BEGO, Bremen, Germany), were used. The chemical compositions of these alloys are presented in Table 1. The alloy groups were further divided into seven subgroups, having eight disc specimens each. These specimens represented the regular fractured surfaces with substantial metal exposure.

The invested wax samples were cast out of these alloys and divested by air-abrasion with Al<sub>2</sub>O<sub>3</sub> (Korox<sup>®</sup>, BEGO, Bremen, Germany) of 110 µm particle size, for 10 s.

Before initiating the bonding procedure, the specimens were embedded in acrylic resin blocks ensuring that one surface of the alloy disc remained

**Table 1** Types and compositions of the alloys tested.

Type	Code	Composition (%)	Brand names	Manufacturer
Noble	Au-Ag-Pt	73.0% Au, 9.2% Ag, 9.0% Pt	Degunorm	Degussa, Hanau, Germany
Base	Ni-Cr-Mo	65.0% Ni, 22.9% Cr, 9.5% Mo	Wiron 99	Bego, Bremen, Germany

uncovered for bonding procedures. The exposed surface of each specimen was ground finished to 1200 grit silicon carbide abrasive (Struers RotoPol 11, Struers A/S, Rodovre, Denmark) and cleaned for 10 min in an ultrasonic bath (Quantrex 90 WT, L and R Manufacturing, Inc., Kearny, NJ, USA) containing ethylacetate and air-dried. Subsequently, surfaces of the disc specimens of both alloy types were air-abraded with 30 µm silica (SiO<sub>2</sub>) coated alumina, Al<sub>2</sub>O<sub>3</sub>, (CoJet<sup>®</sup>, SiOx Sand, ESPE, Seefeld, Germany). The surface conditioning was carried out with circling motions using an intraoral air-abrasion device (Microetcher<sup>™</sup>, Danville Engineering Inc., San Ramon, CA, USA). The nozzle was held approximately 10 mm away from the surface at an angle of 90° for 13 s at a pressure of 2.3 bar and then the specimens were silanized with an MPS silane coupling agent (ESPE<sup>®</sup>-Sil, ESPE, Seefeld, Germany; Lot 119), with a special fine sable brush. This silane contains 3-MPS in >90% ethanol, according to information from the manufacturer.

The silanized surfaces were allowed to react and evaporate for 1, 2, 3, 4, 5, 6, and 7 min, respectively, for each group before the opaquer was applied. Immediately after the silane drying periods, opaquer (Shade A 3,5) (Sinfony<sup>®</sup>, ESPE, Seefeld, Germany; Lot 007) was dispensed at a 1:1 ratio in a glass mixing cup for 45 s using a plastic spatula and was painted on the silanized surface. The polymerization of the opaquer was performed in the light-curing unit (Program 1) (ESPE Visio<sup>®</sup> ALFA Vario, ESPE, Seefeld, Germany), for 2 × 5 s. The hybrid resin composite (Shade A3) (Sinfony<sup>®</sup>, ESPE, Seefeld, Germany; Lot 0029) was applied with an incremental build up on the opaquer layer to a thickness of 2 mm using polyethylene molds. Final polymerization was carried out in the light-curing unit (Program 1) (ESPE Visio<sup>®</sup> BETA Vario, ESPE, Seefeld, Germany), for 15 min under vacuum, as in normal procedures in the dental laboratories.

The specimens were first stored in distilled water at 37 °C for 30 days, and then subjected to thermocycling for 5000 cycles at temperatures alternating between 5 and 55 °C with an immersion time of 30 s. The specimens were mounted in a jig (Bencor Multi-T shear assembly, Danville Engineering Inc., San Ramon, CA, USA) of the universal testing machine (Llyod LRX, Lloyd Instruments Ltd,

Fareham, UK) and the shear force was applied to the adhesive interface until fracture occurred. The specimens were loaded at a crosshead speed of 0.5 mm/min and the stress-strain curve was analysed with Nexygen 2.0 software (Llyod LRX, Lloyd Instruments Ltd, Fareham, UK).

The data were statistically analysed using the analysis of variance (ANOVA) and Fisher's Protected Least Significance Difference (PLSD) methods, due to the significance levels (StatView 5.0, SAS Institute Inc., Cary, NC, USA).

## Results

Analysis of data showed no significant difference in bond strength for silane drying reaction (and evaporation) periods of 1 and 7 min for both base and noble alloys (Degunorm: 5.8–7.4 MPa and Wiron 99: 7.2–10.2 MPa) ( $P = 0.05$ ).

However, significant differences in shear bond strength were observed between noble and base alloys at 2 min (Degunorm: 5.8 MPa, Wiron 99: 9.7 MPa;  $P = 0.0045$ ), 3 min (Degunorm: 7.1 MPa, Wiron 99: 10.18 MPa;  $P = 0.05$ ) and 5 min (Degunorm: 6.0 MPa, Wiron 99: 10.0 MPa;  $P = 0.002$ ) of silane solution drying time intervals (Fig. 1).

## Discussion

The use of silane is a prerequisite to promote the chemical bonding between the silica coated alloy surface and the opaque layer, both providing a chemical link between the resin composite and the alloy and to promote surface wettability. MPS type trialkoxysilane coupling agent is dual functional, i.e. it contains two types of reactive functional groups, all covalently bound to one silicon atom. The three alkoxy groups are (one functional group type) capable of reacting with an inorganic surface containing hydroxyl groups such as a ceramic substrate or metal at one end while at the other end, a polymerizable radical (as methacrylate with a propylene bridge) reacts with the resin composite. Hydrolysed, i.e. reacted with water silanol groups bond chemically either to the hydroxyl groups (-OH) on silicon dioxide (silica) at the ceramic

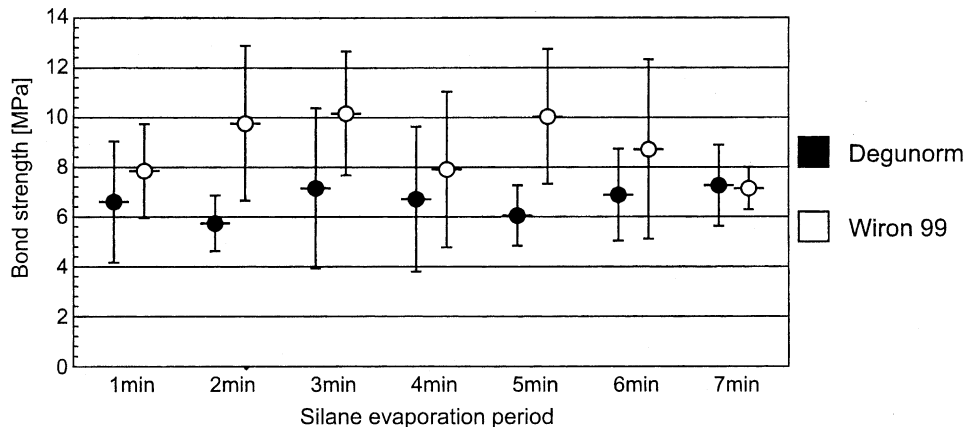


Figure 1 Shear bond strength of Sinfony® to the silica coated base and noble alloys.

matrix, or metal surface through a hydroxyl rich oxide layer, and with elimination of water in the chemical reaction. The silanes enhance the adhesions of the repair resin to the ceramic surface and are said to form a nanomolecular layer.<sup>5,14</sup> However, silanes are also sensitive to humidity either coming from the mouth or from atmospheric conditions in the working environment. Hydrolysis of the silane at elevated temperatures has been previously reported.<sup>15,16</sup> In some clinical cases, the crevicular fluids are a major source of failure.<sup>13</sup> The commercial silane in question, prehydrolyzed MPS, with a functional methacrylic group that is ready to polymerize with the resin composite, should be applied on the silica coated surface and left for 5 min until it has reacted and the excess solution has evaporated from the surface. This study was carried out in order to find out whether shorter or longer silane reaction times have a negative effect on bond strengths in both base and noble alloys. The silane used was in ethanol that evaporates easily. However, in practise, the siloxane layer is thicker, depending on the silane solution concentration, not on the contact time.<sup>17</sup> This might explain the reason why no significant difference was obtained between 1 and 7 min of silane reaction times for both alloys. Conclusions of course, concerning silane solutions other than in ca. 90% ethanol, cannot be drawn.

Although silanes play an important role in the adhesion of the resin composite to the alloys, unfortunately, silanized interfaces do not seem to be very stable. It was reported that bond deterioration occurs even under atmospheric moisture.<sup>18,19</sup> Long-term water storage and/or thermocycling of bonded specimens are accepted methods to simulate aging and to stress the bonding interface. After 5000 thermocycles, the shear bond strength obtained from the base alloy samples presented higher shear bond values

than those of the noble ones at drying times of 1 and 7 min. This suggests that bonding with base alloys, by means of silica coating and silanization, is better than with noble alloys. The base alloy contains chromium and molybdenum that always form a thin oxide layer on their outer surface at room temperature in the air, with hydroxyl groups. In gold alloy, however, only silver may form oxides. Noble alloy surfaces cannot be coupled directly with any silanes but they need a special coupling agent containing thiol (i.e. mercapto, -SH), or thione (=S) groups.<sup>20,21</sup> It is likely that the surface oxide formation is crucial to explain the higher bond strength to base alloy in this study, since the chemical bonding takes place through surface hydroxyl groups. The clinical implication of this data indicates the importance of the underlying alloy type in fixed-partial prostheses for reliable bond strength between the silica coated and silanized surfaces and the composite veneers. However, greater knowledge about the surface characteristics of different alloys after these surface treatments is still needed in order to improve our understanding of the bonding mechanism. For future investigation items, a closer surface analysis (e.g. XPS, photoelectron spectroscopy analysis) of these two materials and the silane layer thickness characterization (e.g. EIS, electrochemical impedance spectroscopy) might give deeper information on a large sample group.

After all drying times, the shear bond strengths obtained between the resin composite and the alloy surfaces obtained, exceeded the suggested bond strength value of 5 MPa (ISO-Norm 10477).<sup>22</sup> The results indicated no necessity to comply with the recommended silane solution evaporation period of at least 5 min for both types of dental alloys. In order to avoid contamination with humidity and to optimise the flow of work, silane treatment time

might be reduced to 1 min that also led to sufficient bond strength according to this norm.

## Conclusions

Within the limitations of this in-vitro study, the following conclusions could be drawn:

1. Drying time of 1 and 7 min for MPS silane on tribochemically silica coated base and noble alloys did not reveal a significant difference in the bond strength of resin composite. Therefore, in order to optimise the flow of work, the drying time of MPS silane could be reduced to 1 min for both base and noble alloys.
2. Bond strength of resin composite to base alloys, after silica coating and silanization was higher than with noble alloys at 2, 3 and 5 min of silane drying time intervals.

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